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Preliminary

Structure Determination of Cellulose Microfibrils in the Cell Wall of *Cladophora*[*1]

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Native cellulose is known to be a composite of varying amount of two distinct allomorphs Iα and Iβ, whose fraction varies depending on the biological origins[1]. The corresponding crystallographic units are characterized as one-chain triclinic and two-chain monoclinic unit cells, respectively[2]. The distribution of these allomorphs in a microfibril, however, has been investigated only on the cellulose microfibrils in the cell wall of *Microdictyon*[2]. Since the cellulose structure exhbits significant biological diversity, we investigated another green algae *Cladophora* to obtain more general idea, employing essentially the same technique used previously[2].

Iα-fraction in *Cladophora* cellulose was estimated to be 0.7 ($\pm$0.01) from FT-IR measurement (0.65 for *Valonia*) with the modified method of Yamamoto *et al.*[3]. In addition the dimension of microfibrils was as large as *Valonia* (ca. 20–30 nm), therefore the sample seemed suitable for the further diffraction analyses as Iα-rich cellulose.

Microcrystalline cellulose suspension was prepared by acid treatment. Individual microfibril was selected to obtain successive microdiffraction patterns along the fiber axis. The electron probe employed throughout this study was ca. 100 nm and all the microscopy was achieved with JEOL-2000EXII operated at 100 kV. From the analyses of all the diagrams, the general concept that the microfibril possesses two domains, namely, one-chain triclinic and two-chain monoclinic crystals, was supported. 100% single-phased diagrams, for instance diagram showing 100% triclinicity, were less frequently observed, and in most cases diagrams contained diffractions from two structures. This means that in *Cladophora*, the two phases are more intimately associated each other than in *Microdictyon*. However, Sugiyama *et al.*[3] used smaller electron probe (20–100 nm) compared to this study, the

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existence of single-phase domain in *Cladophora* has not been completely ruled out yet. The work along this line is in progress by making use of an analytical electron microscope together with imaging plates.

Regarding the manner how these domains are mixed, we could first propose a model as shown in Figure 1b. If one shoots a microfibril along the direction parallel to the diagonal line of its cross section, Fig. 1b is a typical example of the molecular packing, where the molecules are aligned with a distance of 0.39 nm. Typical electron diffraction diagram was shown in Fig. 1a. To our surprise, three meridional reflections (ca. 0.26 nm) showed up in most cases, which are merged into one streaky peak in selected-area diffraction mode. The one in the center was found to be assigned to (004) reflection from monoclinic region, while the other two beside were assigned to ($1\bar{1}4$) from triclinic. On the basis of the previously published crystal models[2], the spot in the left side indicates that the slope of the triclinic ab plane is from the top-right to bottom-left, and that the spot in the right does reverse situation. Therefore the molecular packing that would give the diagram as in Fig. 1a can be schematically drawn as in Fig. 1b. In this projection, the structural difference between

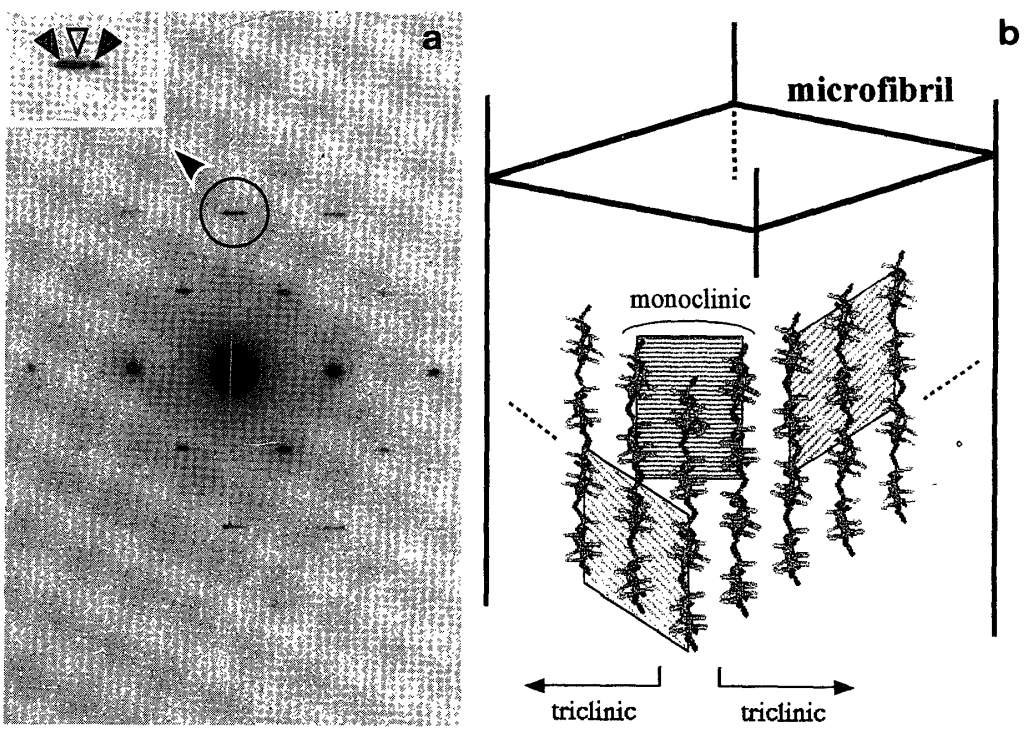

Fig. 1. Diffraction diagram (a) and proposed model (b) as seen in the diagonal direction of its cross section. a : A typical microdiffraction pattern of *Cladophora* cellulose. *Insert*: The central spot is located precisely on the meridian (open arrowhead) which derives from monoclinic structure. The other two spots (solid arrowheads) are from triclinic structure. b : Proposed model showing lateral distribution of two structure, triclinic and monoclinic : Monoclinicity may always appear between two triclinic structure having different slope of ab planes.

triclinic and monoclinic units is quite clear in that the asymmetric unit, i.e. cellobiose, in the triclinic system, shows unidirectional stepping of c/4 between adjacent molecules, whereas in the monoclinic system it does alternations up and down of c/4. Interestingly, one may notice that the packing between two triclinic domains has, in fact, monoclinic characteristics. In conclusion, the two allomorphs in *Cladophora*, were found to coexist intimately and we could first propose the reasonable model explaining the lateral distribution of them, besides the alternative distribution along a single microfibril.

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